Improved Tire Efficiency through Elastomeric Polymers Enhanced with Carbon-Based Nanostructured Materials

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OVERVIEW

Timeline	**Barriers***
• Project start date: January 2016 • Project end date: December 2017	• Development of technologies • Parallel paths (synergistic improvements) • Multiple technologies • Risk aversion • Cost-competitive options **from 2011-2015 VTP MYPP*
Budget (DOE share)	**Partners**
• DOE - $905k	• Oak Ridge National Laboratory • Industrial Partner

OBJECTIVE: To improve tire efficiency and meet DOE's fuel consumption reduction target of 4%, all while maintaining or improving wear characteristics of the tire

"WHY"

- In the United States motorized transportation is mainly implemented by road vehicles.
- The rolling resistance can be responsible for up to 25% of the energy required to drive at highway speeds*.

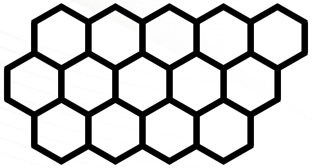
"HOW"

- To reduce the rolling resistance
- To replace existing fillers (such as carbon black and silica) with higher performance materials (viz., graphene and silica nanofibers)
- Reduce hysteretic losses
- Tailor the viscoelastic properties

*Reference: B.E. Lindemuth, ''An overview of tire technology'', Chapter 1 in ''The pneumatic tire'', U.S. Department of Transportation, National Highway Traffic Safety Administration, February 2006

APPROACH: Design of filler material

Graphene nanoplatelets (GnP)



The highest:

Tensile strength

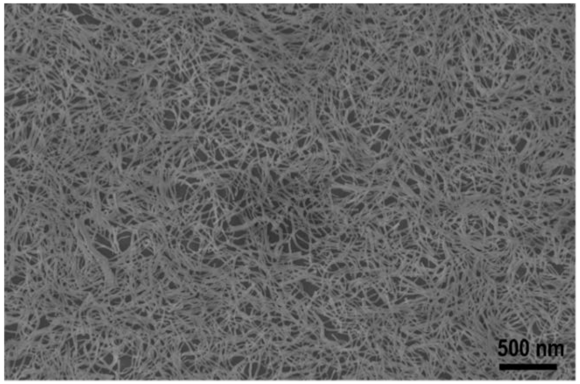
Young's modulus

Specific surface area

High thermal conductivity

+

Silica nanofibers (SNF)



Nanoscale diameter ~100 nm

Flexible

Intrinsically low incidence of defects

High tensile strength

Tailoring the nanoscale properties associated with the physical characteristics of filler-filler and filler-elastomer interactions is an effective route for the design and fabrication of composite tires with unprecedented performance.

Challenges: Particle agglomeration

FY2016 MILESTONES

2nd Quarter of the project

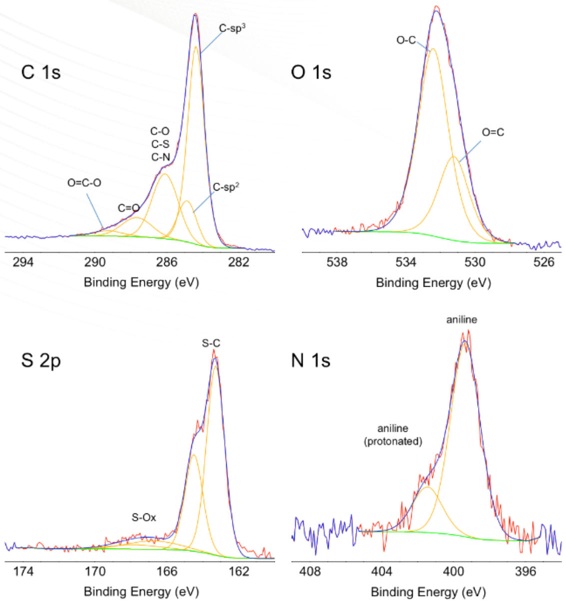
Month /Year	Milestone or Go/No-Go Decision	Description	Status
June 2016	Milestone	Functionalized GnP readily available for dispersion in the rubber matrix	COMPLETE
June 2016	Milestone	The nanofibers should demonstrate modulus values greater than 50 GPa	COMPLETE

Assessment tools

Energy dispersive x-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Atomic force microscopy (AFM)

ACCOMPLISHMENT (1): Functionalized graphene nanoplatelets (GnP)

We have functionalized GnP in order to impart them with the appropriate surface functionalities that will introduce cross-linkages between the GnPs and the elastomer matrix and therefore, will result in a thermodynamically favorable mixture.



Core level spectra fitting analysis of the functionalized samples. The developed functionalization method is reproducible.

Name	GO At. %	rGO At. %	SH-1 At. %	SH-2 At. %
C (sp2)	7.8	7.9	43.3	39.6
C (sp3)	20.8	34.7	4.5	8.7
C-O/C-S/C-N	33.8	24.2	18.0	19.0
O=C-OH	5.6	6.0	1.3	1.8
C=O	0.0	0.0	5.7	6.6
O-C	23.3	22.3	8.6	11.4
O=C	6.5	3.5	9.5	5.0
S-O	1.2	0.2	0.5	0.5
H-S-C	0.0	0.0	3.4	3.7
N-Aniline	0.0	0.0	2.5	2.5
N-Aniline+	0.0	0.0	0.7	0.6
Si-O	0.9	1.2	2.1	0.8

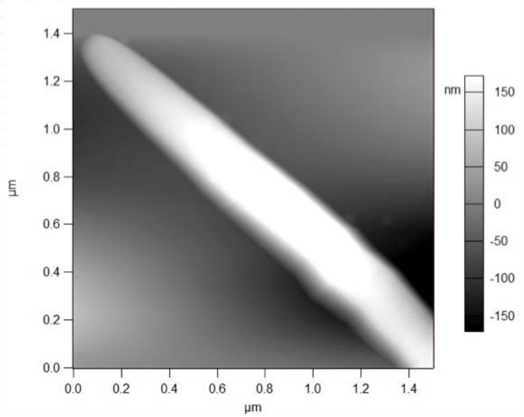
Surface composition according to the core level spectra analysis.

Key findings:

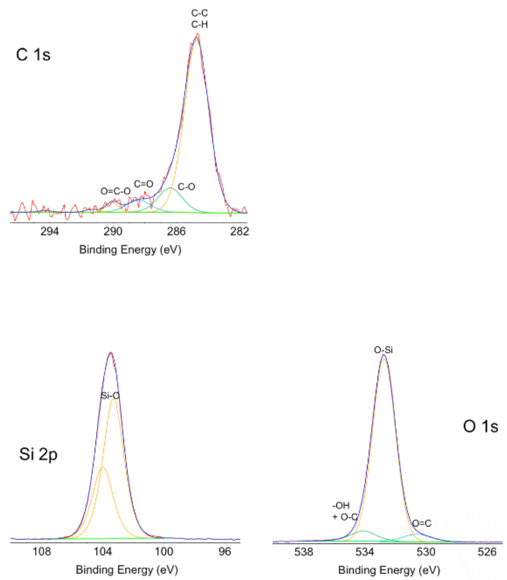
- The GnP fillers were successfully functionalized. The functionalization of the fillers was uniform.
- The concentration of the introduced surface functionality is 3.4 at.%.
- The mixing temperature was defined in order not to degrade the chemical functionalities on the surface of the fillers.

ACCOMPLISHMENT (2): Synthesize silica nanofibers with high modulus value

According to nanoindentation techniques the modulus values of the silica nanofibers are greater than 50 GPa.



AFM image of the silica nanofiber



Silica nanofibers

Name	At. %
C1s_C-C	2.6
C1s_C-O	0.4
C1s_C=O	0.2
O (O=C)	2.9
O (O-Si)	55.0
O (O-H)	3.7
Si (Si-O)	33.1
Na	2.0

XPS core level spectra analysis and the corresponding surface composition of the synthesized silica nanofibers.

Key findings:

- The Young's modulus value of the synthesized silica nanofibers is greater than 50 GPa.
- The high modulus value indicate that there are no defects in the structure of the nanofibers.
- The SiO_2 content on the surface of the nanofibers is approximately 90%.

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FY2016 MILESTONES

3rd Quarter of the project

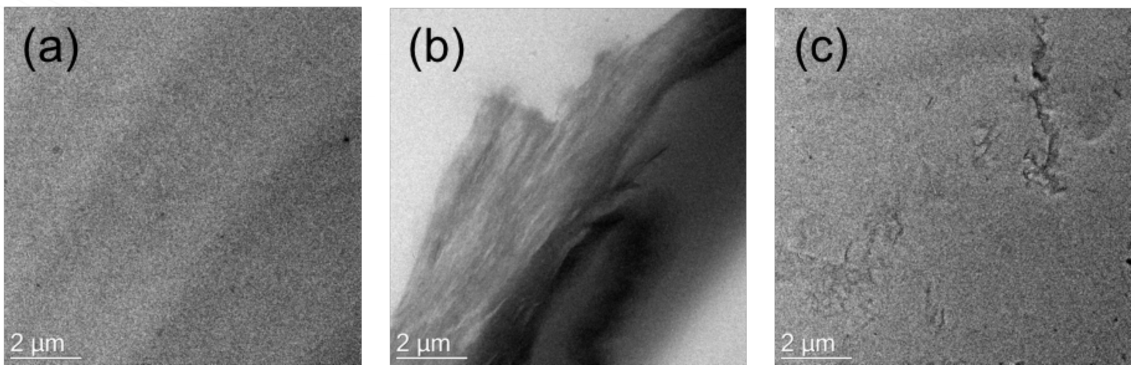
Month /Year	Milestone or Go/No-Go Decision	Description	Status
Sept. 2016	Milestone	Define the processing conditions in order to well-disperse GnP in the rubber matrix	COMPLETE

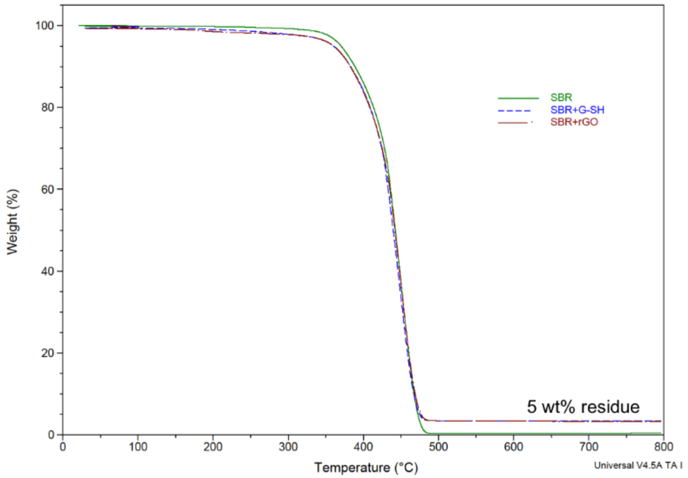
Assessment tools

Brabender mixing equipment, Thermogravimetric analysis (TGA), Rheology, Transmission electron microscopy (TEM), Dynamic mechanical analysis (DMA)

ACCOMPLISHMENT (1): Improved dispersion of the graphene nanoplatelets (GnP)

The agglomerated structures are more pronounced in the SBR/rGO system that has no functional groups on the surface of the graphene.



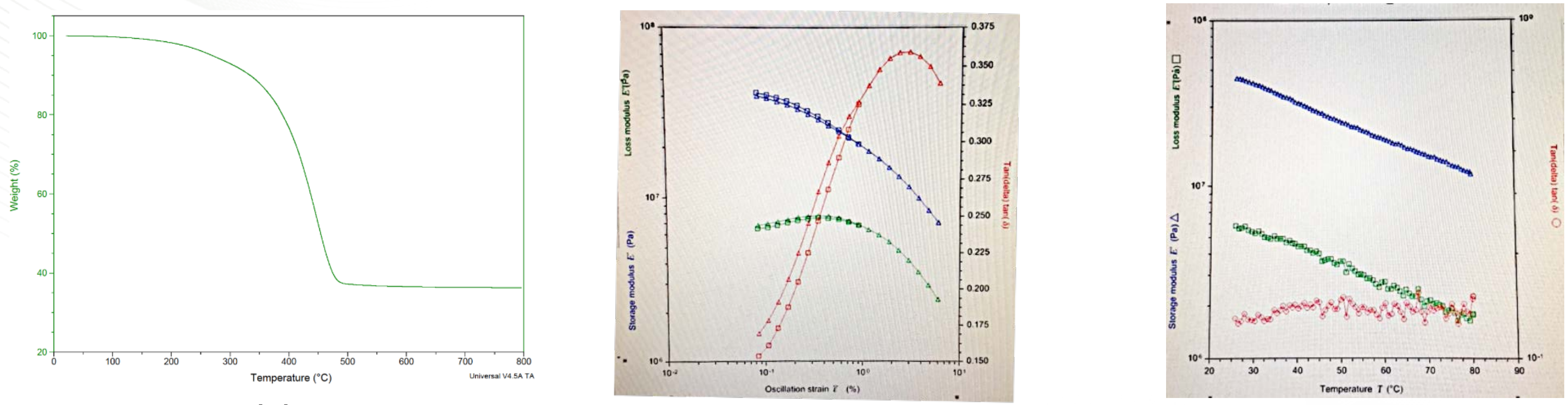


TEM images of the **(a)** unfilled SBR, **(b)** SBR filled with 5wt% rGO and **(c)** 5wt% SHGO.

TGA thermograms of the unfilled SBR, and SBR filled with 5wt% rGO and 5wt% SHGO.

ACCOMPLISHMENT (2): Establish baseline values

The tand values correspond to the hysteretic losses and are related to the rolling resistance of the tire.



(a) (b) (c)

Thermomechanical analysis of the baseline composite elastomer. **(a)** TGA analysis, **(b)** DMA oscillation strain sweep at fixed frequency 10Hz, **(c)** DMA temperature sweep at a 10Hz.

Key findings:

- The processing conditions to disperse the fillers in the elastomer matrix were identified.
- The analysis of the samples showed good dispersion properties.
- The functionalized graphene fillers showed improved dispersion properties in the nanoscale compared to the non-functionalized graphene fillers.
- We have established baseline values for the thermomechanical performance of composite elastomer that is currently being used in the manufacturing of tires.
- ORNL generated Safety Data Sheets for the in-house synthesized graphene fillers.

FY2017 MILESTONES

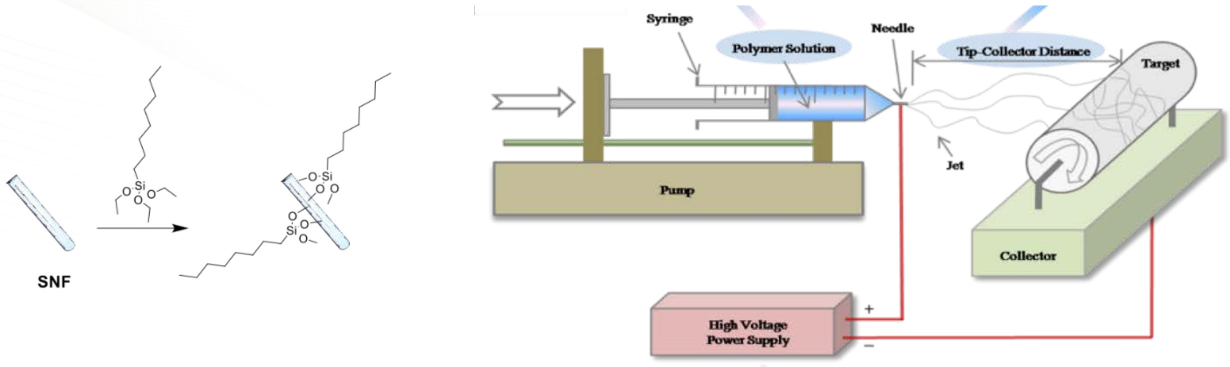
4th Quarter of the project

Month /Year	Milestone or Go/No-Go Decision	Description	Status
January 2017	Milestone	Define the silica nanofiber volume fraction in order to increase the tear resistance	COMPLETE
January 2017	Milestone	Define the GnP Volume fraction in order to achieve 4% fuel saving	COMPLETE
January 2017	Milestone	Increase in the tear resistance of the rubber composite	COMPLETE
January 2017	Go/No-Go Gate	Demonstrate the feasibility to fabricate composite rubber materials that demonstrate reduced hysteretic losses (sufficient to achieve at least 4% fuel savings), and at the same time exhibit improved tear strength	COMPLETE

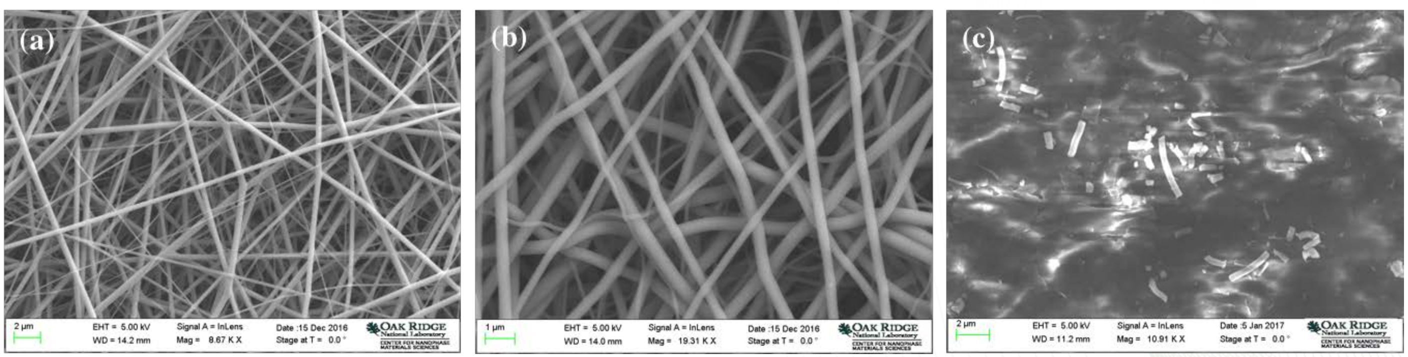
Assessment tools

X-ray diffraction (XPD), Thermogravimetric analysis (TGA), Scanning electron microscopy (SEM), Dynamic mechanical analysis (DMA)

ACCOMPLISHMENT (1): Define silica nanofiber volume fraction



Schematic images of the modified silica nanofibers and the electrospinning process.



(a), (b) SEM images of the scalable electrospun silica nanofibers synthesized at ORNL, **(c)** ground silica nanofibers.

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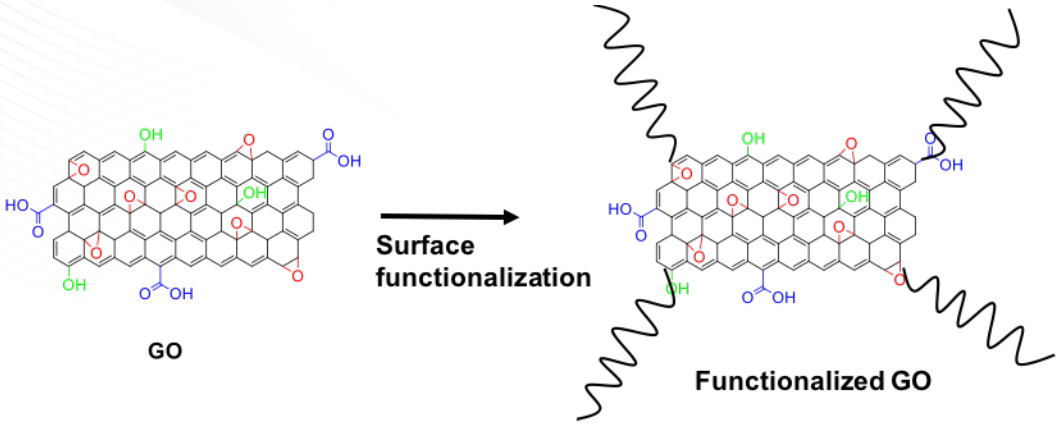
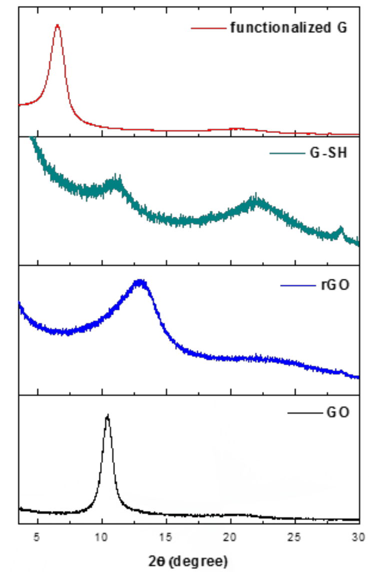
ACCOMPLISHMENT (2): Define GnP volume fraction

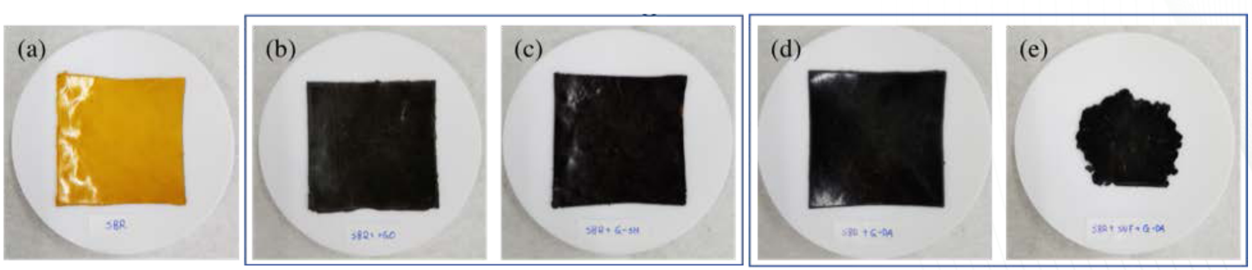


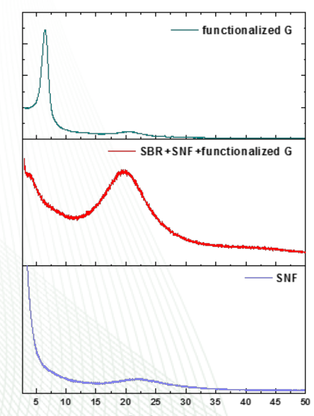
(a)



(b)

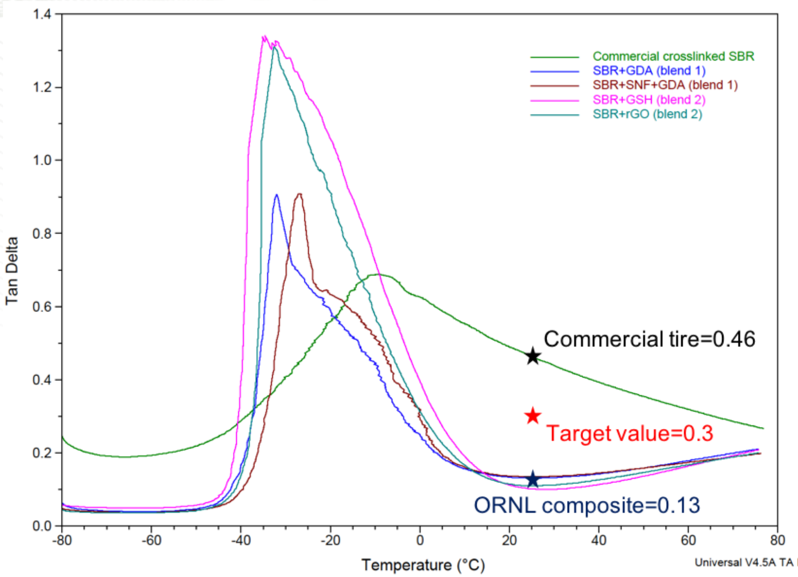
(a) Schematic images of surface modified graphene (G-DA). **(b)** XRD spectrum of graphene oxide and modified graphene.



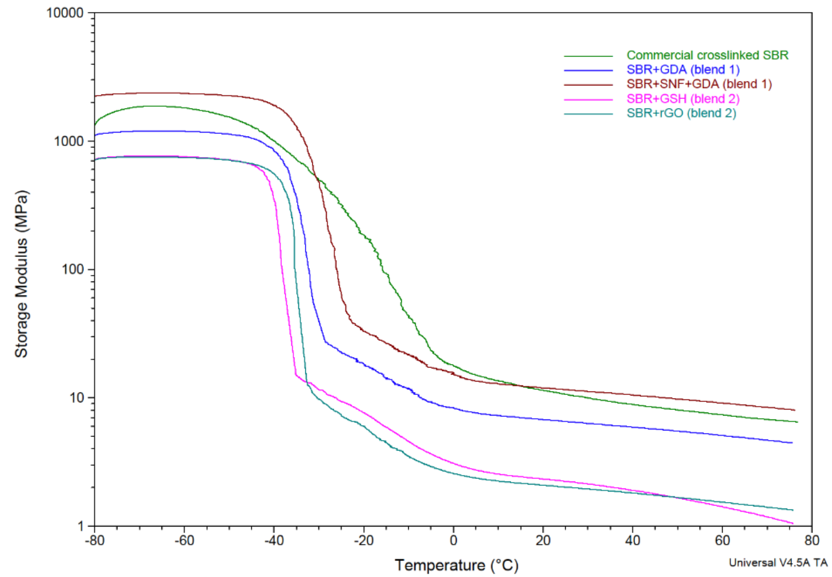


Composite samples based on silica nanofibers and graphene modified **(a)** SBR, **(b)** SBR+rGO, **(c)** SBR+G-SH, **(d)** SBR+G-DA, and **(e)** SBR+SNF+G-DA.

ACCOMPLISHMENT (3): Feasibility to achieve at least 4% fuel savings



Tand values of the synthesized composites at a broad temperature range. The respective values of a commercial elastomer that was provided by our industrial partner is also included.



Modulus values of the synthesized composites at a broad temperature range. The respective values of a commercial elastomer that was provided by our industrial partner is also included.

Key findings:

- The functionalized graphene nanoplatelets showed good dispersion in the polymer elastomer.
- Electrospun silica nanofibers (SNF) using a scalable method were successfully synthesized and functionalized.
- The combination of SNF and GnP fillers synergistically improved the mechanical performance of the elastomer.
- It is feasible to achieve 4% reduction in the fuel efficiency and at the same time to enhance the mechanical performance of the tire. The target tand value is 0.3. Our non-crosslinked composites exhibit tand value 0.13 and at the same time improve up to 20% the mechanical properties of the elastomer.

Summary

- **Relevance:**

Supports major goals of the Vehicle Technologies Program (VTP)

Tires for Improved Fuel Efficiency

– Reduce the rolling resistance.

– Improve the fuel economy (mpg) of vehicles.

– A 25-30% reduction in the rolling resistance will result in improvement in fuel mileage of up to 4%*.

– Estimates for the California Energy Commission have indicated that about 1.5% to 4.5% of gasoline use could be saved if all replacement tires in the U.S. were low rolling resistance tires*.

– Improve the tear resistance.

Addresses the following Barriers:

– **Development of technologies**: Design of new materials with tailored properties.

– **Parallel paths (synergistic improvements)**: Combines new materials with complementary properties.

– **Risk aversion**: Development of two types of filler material that will provide parallel improvements.

– **Cost-competitive options**: Enables fabrication techniques that can be scaled in manufacturing environment. Graphene filler material can potentially be fabricated easily and cheaply from bulk graphite.

*Reference: Vehicle Technologies Multi-Year Program Plan 2011-2015:

http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/vt_mypp_2011-2015.pdf

Summary

- **Approach:** Tailoring the nanoscale properties associated with the physical characteristics of filler-filler and filler-elastomer interactions is an effective route for the design and fabrication of composite tires with unprecedented performance.

- **Collaborations:** Major tire manufacturer.

- **Technical Accomplishments:**
  - Develop new filler material with tailored surface functionalities.
  - Demonstrate the feasibility to fabricate composite elastomer materials that demonstrate reduced hysteretic losses (sufficient to achieve at least 4% fuel savings), and at the same time exhibit improved tear strength.

- **Future Work:**
  - Find suitable industrial partners for the scale-up of the developed fillers for the pilot scale production of tires.

Any proposed future work is subject to change based on funding levels

Future Work - Project Phase II

Month /Year	Milestone or Go/No-Go Decision	Description	Status
March 2017	Milestone	Produce GnP and silica nanofibers that will be used to manufacture tires industrial protocols	Ongoing
June 2017	Milestone	Deliver to industrial partner scaled-up functionalized fillers for tire manufacturing	Ongoing
September 2017	Milestone	Cured tires with tread components containing the ORNL-provided nanoparticles	Ongoing
September 2017	Milestone	Meet DOE's fuel consumption reduction target of 4%, all while maintaining or improving wear characteristics of the tire	Ongoing
December 2017	Milestone	Testing results on composite tires and final report	Ongoing

Any proposed future work is subject to change based on funding levels

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